

(12) UK Patent Application (19) GB (11) 2 290 745 (13) A

(43) Date of A Publication 10.01.1996

(21) Application No 9512540.7

(22) Date of Filing 20.06.1995

(30) Priority Data

(31) 270065

(32) 01.07.1994

(33) US

(71) Applicant(s)

Ciba-Geigy AG

(Incorporated in Switzerland)

Klybeckstrasse 141, CH-4002 Basle, Switzerland

(72) Inventor(s)

James Harold Botkin

Joseph Suhadolnik

(74) Agent and/or Address for Service

Thomas Sharman

Ciba-Geigy plc, Patent Department, Central Research,
Hulley Road, MACCLESFIELD, Cheshire, SK10 2NX,
United Kingdom

(51) INT CL⁶

B29C 47/06 67/24, B32B 27/36 // B29K 23:00 27:06
33:04 55:02 67:00 69:00 71:00 73:00, B29L 7:00

(52) UK CL (Edition O)

B5A AC AT17P A1G10 A1G2 A1R314C1C A1R314C1D
A1R314C1E A1R314C1F A1R314C1S A1R314C1X
A1R314C6 A1R400 A20T17

B5N N195 N196 N207 N209 N21Y N223 N225 N227
N229 N237 N24X N255 N257 N259 N26X N261 N264
N266 N2708 N2730 N2732 N2736 N281 N283 N287
N29Y N293 N295 N297 N331 N36X N37X N374 N377
N38X N381 N383 N398 N401 N408 N409 N41Y N455
N457 N463 N465 N466 N469 N470 N474 N477 N478
N479 N485 N488 N518 N519 N57Y N584 N59Y N603
N611 N62X N62Y N648 N649 N658 N66X N66Y N661
N662 N670 N672 N680 N771

(56) Documents Cited

GB 2028228 A GB 1572728 A GB 1444562 A
US 5288778 A US 3244708 A

(58) Field of Search

UK CL (Edition N) B5A AC AT17P
INT CL⁶ B29C 47/06 67/24
ONLINE: WPI

(54) Coextruded stabilised laminated thermoplastics

(57) Thermoplastic articles, preferably of polycarbonate, are advantageously stabilized by selected o-hydroxyphenyl-s-triazine UV absorbers concentrated in the outer surface or coating layers of the article prepared by coextrusion techniques.

GB 2 290 745 A

STABILIZED LAMINATED THERMOPLASTICS

This invention relates to an improved process for producing coated thermoplastic articles, preferably via coextrusion, wherein the coating layers contain selected o-hydroxy-phenyl-s-triazine UV absorbers, and to the stabilized articles thus produced.

Background of the Invention

The use of various types of UV absorbers in the stabilization of polymers is well known. These stabilizers function by absorbing incident UV radiation and dispersing the absorbed energy in a nondestructive manner. Concentration of the UV absorber near the surface of the polymer to prevent penetration of UV light is, therefore, considered to be more efficient and economical than dispersion of the UV absorber throughout the bulk of the polymer.

The protection of aromatic polycarbonates from UV light is a particular problem as the polymer itself absorbs significant amounts of high energy light and is known to become quickly yellow and hazy. Aside from their strength and toughness, polycarbonates derive much of their value from their excellent optical properties, i.e. low color and high clarity. Therefore, protection against UV radiation at the surface of a polymer like polycarbonate, where most of the light would be absorbed, becomes vital.

It is of course obvious that any color imparted to the polymer composition by the stabilizer itself must be as little as possible.

A number of methods have been developed to concentrate UV absorbers near or at the surface of polymeric materials. These include surface impregnation (see U.S. Patent Nos. 3,309,220, 3,043,709, 4,861,664 and 4,937,026) and coating a plastic article with solutions containing thermoplastic resins and UV absorbers (see U.S. Patent Nos. 4,668,588 and 4,353,965). Both techniques suffer from significant drawbacks including requiring additional processing steps (i.e. applying, drying or curing), and encounter the difficulties associated with the handling of large processed articles. An additional drawback, particularly relevant to polycarbonate sheet production, is the detrimental effect such post addition treatment would have on the surface of the polymeric substrate.

Coextrusion is a well recognized method of producing laminated thermoplastic materials by simultaneously extruding various numbers of layers which form a single composite material. U.S. Patent No. 4,540,623 describes coextruded materials of at least forty layers. Other methods produce as few as two or three different layers.

The resins employed in each layer may be the same, different e.g. polypropylene or polyacrylate or polycarbonate or be different types of similar resin such as two different aromatic polycarbonates.

Likewise, the types and amounts of additives employed in each layer may vary significantly. Typical additives include dyes, pigments, antioxidants, processing and UV stabilizers and glass fillers.

The use of coextrusion to produce a photo-stable article by incorporating a light absorbing layer at or near the surface of the laminate has received attention. Of particular importance is the protection of a polycarbonate core layer via such a process.

In EP 110,221, a polycarbonate core layer is protected with a thin polycarbonate layer which contains a high concentration of UV absorber. However, the UV absorbers used are volatile, especially under extrusion conditions, and loss and migration from the polymer composition may occur.

To prevent additive exudation, a third capping or barrier layer is incorporated which contains little or no volatile additive. In U.S. Patent No. 4,707,393 a permanent layer of poly(methyl methacrylate) (PMMA) or PMMA composite is coextruded on top of the two polycarbonate layers. EP 345,884 describes the use of a removable barrier layer.

Recently, U.S. Patent No. 5,108,835 teaches that the exudation problem of EP 110,221 can be overcome by incorporating certain low volatility bisbenzotriazole UV absorbers into the UV absorbing layer. These non-migrating UV absorbers make the capping layer of U.S. Patent No. 4,707,393 or EP 345,884 unnecessary. This process claims the advantages of simplified production and perhaps more importantly, improved UV and weather stabilization of the thermoplastic moldings produced.

Canadian Patent Appl. 2,002,177 discloses a special polymethacrylate coating for

aromatic polycarbonate which may be applied via coextrusion. This coating could contain a wide variety of UV absorbers for photostabilization of the polymers. However, the focus of this patent is to provide polycarbonate compatible polymethacrylate and provides no guidance toward the selection of UV absorber. The specific class of o-hydroxyphenyl-s-triazines of the instant invention is not discussed.

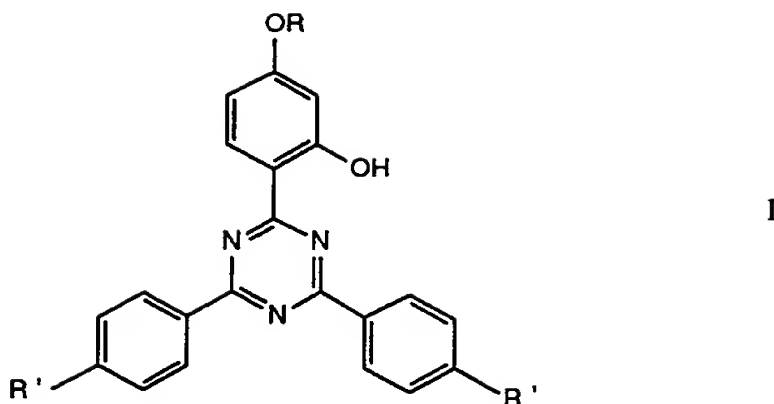
U.S. Patent No. 3,244,708 described UV absorbers corresponding to the compounds of formula I. U.S. Patent No. 5,288,778 describes the use of these o-hydroxyphenyl-s-triazine UV absorbers as stabilizers for polymers having heteroatoms in the main polymer chain, by virtue of significant performance advantages over other o-hydroxyphenyl-s-triazines including the generic description of the use of such compounds in the outer layer of a multilayer polymer system without any specific details.

U.S. Patent No. 5,306,456 discloses the use of bisbenzophenones as the UV absorbers in the outer surface or coating layers of an articles by coextrusion techniques.

The present invention offers an improvement over the existing prior art in that it not only provides the same simplification in production of photostabilized double walled thermoplastics found in U.S. Patent No. 5,108,835, but also provides a laminated thermoplastic article with improved weathering resistance and lower color development than is currently available with the use of other classes of UV absorbers such as the bisbenzotriazoles or bisbenzophenones.

Detailed Disclosure

More specifically this invention pertains to a process whereby a multi-layered, coextruded thermoplastic article is produced, characterized by the incorporation into an outer UV absorbing coating layer of a selected o-hydroxyphenyl-s-triazine UV stabilizer of formula I



wherein

R is hydrogen, C₁-C₁₈alkyl, C₂-C₆alkyl substituted by halogen or by C₁-C₁₂alkoxy, or R is benzyl, and

R' is hydrogen or methyl.

Preferably, R is C₁-C₁₂alkyl or benzyl; most preferably R is C₃-C₆alkyl.

Preferably R' is hydrogen.

The application of surface layers via coextrusion takes place in a known manner in known coextrusion equipment as taught in U.S. Patent Nos. 3,487,505 and 3,557,265.

The invention also relates to thermoplastic articles coated with a thermoplastic layer 5-500 microns thick, in which said layer contains 0.1% to 20% by weight of o-hydroxyphenyl-s-triazine UV absorbers of formula I as defined above. Preferred concentrations of UV absorber are 1% to 15% by weight; most preferred concentrations of 2% to 10% by weight.

The UV absorbers of the instant invention may be incorporated into the thermoplastics of the surface layer by standard methods such as dry mixing the additives with granular resin prior to extruding.

The UV absorbing layer may be applied to one or both sides of the thermoplastic article.

Laminated thermoplastic articles corresponding to the present invention which

contain additional layers such as a water resistant layer as found in U.S. Patent No. 4,992,322 are also within the scope of the present invention.

The core layer and the coating layer may be of the same thermoplastic resin or different thermoplastic resins. These resins include aromatic polycarbonates, polyesters, polyester carbonates, polyphenylene oxide, polyvinyl chloride, polypropylene, polyethylene, polyacrylates, polymethacrylates and copolymers and blends such as styrene and acrylonitrile on polybutadiene and styrene with maleic anhydride.

The preferred resins are polycarbonates based on dihydric phenols such as 2,2-bis-(4-hydroxyphenyl)propane (bisphenol A); 2,4-bis-(4-hydroxyphenyl)-2-methylbutane; 1,1-bis-(4-hydroxyphenyl)cyclohexane; 2,2-bis-(3-chloro-4-hydroxyphenyl)propane; 4,4'-sulfonyldiphenol; and 1,1-bis-(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane.

Also preferred are polycarbonate copolymers incorporating two or more phenols, branched polycarbonates wherein a polyfunctional aromatic compound is reacted with the dihydric phenol(s) and carbonate precursor, and polymer blends of which polycarbonate comprises a significant portion of the blend.

The most preferred resins for both layers are polycarbonates based on bisphenol A.

Other conventional additives such as reinforcing agents and fillers, flame retardants, dyes, pigments, lubricants, and stabilizers added to protect the polymer during processing or against subsequent thermal degradation may also be present in either or both of the layers. Processing/thermal stabilizers include, for example, the hindered phenol antioxidants, organic phosphites, phosphates, phosphonates and thioethers.

The resulting stabilized polycarbonate compositions of the instant invention may optionally also contain from about 0.01 to about 5%, preferably from about 0.025 to about 2%, and especially from about 0.1 to about 1% by weight of various conventional additives, such as the materials listed below, or mixtures thereof.

When the thermoplastic resin is a polycarbonate or a polycarbonate copolymer, some of the coadditives listed below are to be avoided. These include antioxidants of group 1.3, group 1.6; 1-(3,5-di-tert-butyl-4-hydroxyanilino)-3,5-di(octylthio)-s-triazine and N,N'-hexamethylene-bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamamide); light

stabilizers of group 2.6; compounds of group 5 which are mercapto-benzimidazole, the zinc salt of 2-mercapto-benzimidazole and zinc dibutyl-dithiocarbamate; and compounds of group 6, group 7 and group 9.

1. Antioxidants

1.1. Alkylated monophenols, for example,

2,6-di-tert-butyl-4-methylphenol
2-tert-butyl-4,6-dimethylphenol
2,6-di-tert-butyl-4-ethylphenol
2,6-di-tert-butyl-4-n-butylphenol
2,6-di-tert-butyl-4-i-butylphenol
2,6-di-cyclopentyl-4-methylphenol
2-(α -methylcyclohexyl)-4,6-dimethylphenol
2,6-di-octadecyl-4-methylphenol
2,4,6-tri-cyclohexylphenol
2,6-di-tert-butyl-4-methoxymethylphenol

1.2. Alkylated hydroquinones, for example,

2,6-di-tert-butyl-4-methoxyphenol
2,5-di-tert-butyl-hydroquinone
2,5-di-tert-amyl-hydroquinone
2,6-diphenyl-4-octadecyloxyphenol

1.3. Hydroxylated thiodiphenyl ethers, for example,

2,2'-thio-bis-(6-tert-butyl-4-methylphenol)
2,2'-thio-bis-(4-octylphenol)
4,4'-thio-bis-(6-tert-butyl-3-methylphenol)
4,4'-thio-bis-(6-tert-butyl-2-methylphenol)

1.4. Alkylidene-bisphenols, for example,

2,2'-methylene-bis-(6-tert-butyl-4-methylphenol)

2,2'-methylene-bis-(6-tert-butyl-4-ethylphenol)
2,2'-methylene-bis-[4-methyl-6-(α -methylcyclohexyl)-phenol]
2,2'-methylene-bis-(4-methyl-6-cyclohexylphenol)
2,2'-methylene-bis-(6-nonyl-4-methylphenol)
2,2'-methylene-bis-[6-(α -methylbenzyl)-4-nonylphenol]
2,2'-methylene-bis-[6-(α,α -dimethylbenzyl)-4-nonylphenol]
2,2'-methylene-bis-(4,6-di-tert-butylphenol)
2,2'-ethylidene-bis-(4,6-di-tert-butylphenol)
2,2'-ethylidene-bis-(6-tert-butyl-4-isobutylphenol)
4,4'-methylene-bis-(2,6-di-tert-butylphenol)
4,4'-methylene-bis-(6-tert-butyl-2-methylphenol)
1,1-bis-(5-tert-butyl-4-hydroxy-2-methylphenyl)-butane
2,6-di-(3-tert-butyl-5-methyl-2-hydroxybenzyl)-4-methylphenol
1,1,3-tris-(5-tert-butyl-4-hydroxy-2-methylphenyl)-butane
1,1-bis-(5-tert-butyl-4-hydroxy-2-methylphenyl)-3-n-dodecylmercaptobutane
ethyleneglycol bis-[3,3-bis-(3'-tert-butyl-4'-hydroxyphenyl)-butyrate]
di-(3-tert-butyl-4-hydroxy-5-methylphenyl)-dicyclopentadiene
di-[2-(3'-tert-butyl-2'-hydroxy-5'-methyl-benzyl)-6-tert-butyl-4-methylphenyl]
terephthalate.

1.5. Benzyl compounds, for example,

1,3,5-tri-(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene
di-(3,5-di-tert-butyl-4-hydroxybenzyl) sulfide
3,5-di-tert-butyl-4-hydroxybenzyl-mercapto-acetic acid isooctyl ester
bis-(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)dithiol terephthalate
1,3,5-tris-(3,5-di-tert-butyl-4-hydroxybenzyl) isocyanurate
1,3,5-tris-(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl) isocyanurate
3,5-di-tert-butyl-4-hydroxybenzyl-phosphoric acid dioctadecyl ester
3,5-di-tert-butyl-4-hydroxybenzyl-phosphoric acid monoethyl ester, calcium-salt

1.6. Acylaminophenols, for example,

4-hydroxy-lauric acid anilide
4-hydroxy-stearic acid anilide
2,4-bis-octylmercapto-6-(3,5-tert-butyl-4-hydroxyanilino)-s-triazine

octyl-N-(3,5-di-tert-butyl-4-hydroxyphenyl)-carbamate

1.7. Esters of β -(3,5-di-tert-butyl-4-hydroxyphenyl)-propionic acid with monohydric or polyhydric alcohols, for example,

methanol	diethylene glycol
octadecanol	triethylene glycol
1,6-hexanediol	pentaerythritol
neopentyl glycol	tris-hydroxyethyl isocyanurate
thiodiethylene glycol	di-hydroxyethyl oxalic acid
	diamide

1.8. Esters of β -(5-tert-butyl-4-hydroxy-3-methylphenyl)-propionic acid with monohydric or polyhydric alcohols, for example,

methanol	diethylene glycol
octadecanol	triethylene glycol
1,6-hexanediol	pentaerythritol
neopentyl glycol	tris-hydroxyethyl isocyanurate
thiodiethylene glycol	di-hydroxyethyl oxalic acid
diamide	

1.9. Amides of β -(3,5-di-tert-butyl-4-hydroxyphenyl)-propionic acid for example,

N,N'-di-(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)-hexamethylenediamine
N,N'-di-(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)-trimethylenediamine
N,N'-di-(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)-hydrazine

2. UV absorbers and light stabilizers

2.1. 2-(2'-Hydroxyphenyl)-benzotriazoles, for example, the 5'-methyl-, 3',5'-di-tert-butyl-, 5'-tert-butyl-, 5'-(1,1,3,3-tetramethylbutyl)-, 5-chloro-3',5'-di-tert-butyl-, 5-chloro-3'-tert-butyl-5'-methyl-, 3'-sec-butyl-5'-tert-butyl-, 4'-octoxy, 3',5'-di-tert-amyl-, 3',5'-bis-(α,α -dimethylbenzyl)-, 3'-tert-butyl-5'-(2-(ω -hydroxy-octa-(ethyleneoxy)carbonyl-ethyl)-, 3'-dodecyl-5'-methyl-, and 3'-tert-butyl-5'-(2-octyloxycarbonyl)ethyl-, and

dodecylated-5'-methyl derivatives.

2.2. 2-Hydroxy-benzophenones, for example, the 4-hydroxy-, 4-methoxy-, 4-octoxy-, 4-decyloxy-, 4-dodecyloxy-, 4-benzyloxy, 4,2',4'-trihydroxy- and 2'-hydroxy-4,4'-dimethoxy derivatives.

2.3. Esters of optionally substituted benzoic acids for example, phenyl salicylate, 4-tert-butylphenyl salicylate, octylphenyl salicylate, dibenzoylresorcinol, bis-(4-tert-butylbenzoyl)-resorcinol, benzoylresorcinol, 3,5-di-tert-butyl-4-hydroxybenzoic acid 2,4-di-tert-butylphenyl ester and 3,5-di-tert-butyl-4-hydroxybenzoic acid hexadecyl ester.

2.4. Acrylates, for example, α -cyano- β,β -diphenylacrylic acid ethyl ester or isooctyl ester, α -carbomethoxy-cinnamic acid methyl ester, α -cyano- β -methyl-p-methoxy-cinnamic acid methyl ester or butyl ester, α -carbomethoxy-p-methoxy-cinnamic acid methyl ester, N-(β -carbomethoxy- β -cyanovinyl)-2-methyl-indoline.

2.5. Nickel compounds, for example, nickel complexes of 2,2'-thio-bis-[4-(1,1,3,3-tetramethylbutyl)-phenol], such as the 1:1 or 1:2 complex, optionally with additional ligands such as n-butylamine, triethanolamine or N-cyclohexyl-diethanolamine, nickel dibutyldithiocarbamate, nickel salts of 4-hydroxy-3,5-di-tert-butylbenzylphosphonic acid monoalkyl esters, such as of the methyl, ethyl or butyl ester, nickel complexes of ketoximes such as of 2-hydroxy-4-methyl-phenyl undecyl ketoxime, nickel complexes of 1-phenyl-4-lauroyl-5-hydroxy-pyrazole, optionally with additional ligands.

2.6. Sterically hindered amines, for example bis-(2,2,6,6-tetramethylpiperidyl) sebacate, bis-(1,2,2,6,6-pentamethylpiperidyl) sebacate, n-butyl-3,5-di-tert-butyl-4-hydroxybenzyl malonic acid bis-(1,2,2,6,6-pentamethylpiperidyl)ester, condensation product of 1-hydroxyethyl-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid, condensation product of N,N'-(2,2,6,6-tetramethylpiperidyl)-hexamethylenediamine and 4-tert-octylamino-2,6-dichloro-s-triazine, tris-(2,2,6,6-tetramethylpiperidyl)-nitrilotriacetate, tetrakis-(2,2,6,6-tetramethyl-4-piperidyl) 1,2,3,4-butanetetracarboxylate, 1,1'-(1,2-ethanediyl)-bis-(3,3,5,5-tetramethylpiperazinone), bis(1-octyloxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate.

2.7. Oxalic acid diamides, for example, 4,4'-di-octyloxy-oxanilide, 2,2'-di-octyloxy-

5,5'-di-tert-butyl-oxanilide, 2,2'-di-dodecyloxy-5,5'-di-tert-butyl-oxanilide, 2-ethoxy-2'-ethyl-oxanilide, N,N'-bis (3-dimethylaminopropyl)-oxalamide, 2-ethoxy-5-tert-butyl-2'-ethyloxanilide and its mixture with 2-ethoxy-2'-ethyl-5,4'-di-tert-butyloxanilide and mixtures of ortho- and para-methoxy- as well as of o- and p-ethoxy-disubstituted oxanilides.

2.8. Hydroxyphenyl-s-triazines, for example 2,6-bis-(2,4-dimethylphenyl)-4-(2-hydroxy-4-octyloxyphenyl)-s-triazine;

2,6-bis-(2,4-dimethylphenyl)-4-(2,4-dihydroxyphenyl)-s-triazine;

2,4-bis(2,4-dihydroxyphenyl)-6-(4-chlorophenyl)-s-triazine; 2,4-bis[2-hydroxy-4-(2-hydroxyethoxy)phenyl]-6-(4-chlorophenyl)-s-triazine; 2,4-bis[2-hydroxy-4-(2-hydroxy-4-(2-hydroxyethoxy)phenyl)-6-(2,4-dimethylphenyl)-s-triazine;

2,4-bis[2-hydroxy-4-(2-hydroxyethoxy)phenyl]-6-(4-bromophenyl)-s-triazine;

2,4-bis[2-hydroxy-4-(2-acetoxyethoxy)phenyl]-6-(4-chlorophenyl)-s-triazine,

2,4-bis(2,4-dihydroxyphenyl)-6-(2,4-dimethylphenyl)-s-triazine.

3. Metal deactivators, for example, N,N'-diphenyloxalic acid diamide, N-salicylal-N'-salicyloylhydrazine, N,N'-bis-salicyloylhydrazine, N,N'-bis-(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)-hydrazine, 3-salicyloylamino-1,2,4-triazole, bis-benzylidene-oxalic acid dihydrazide.

4. Phosphites and phosphonites, for example, triphenyl phosphite, diphenylalkyl phosphites, phenyldialkyl phosphites, tri-(nonylphenyl) phosphite, trilauryl phosphite, trioctadecyl phosphite, di-stearyl-pentaerythritol diphosphite, tris-(2,4-di-tert-butylphenyl) phosphite, di-isodecylpentaerythritol diphosphite, di-(2,4-di-tert-butylphenyl)pentaerythritol diphosphite, tristearyl-sorbitol triphosphite, tetrakis-(2,4-di-tert-butylphenyl) 4,4'-diphenylenediphosphonite.

5. Compounds which destroy peroxide, for example, esters of β -thiodipropionic acid, for example the lauryl, stearyl, myristyl or tridecyl esters, mercapto-benzimidazole or the zinc salt of 2-mercaptobenzimidazole, zinc dibutyl-dithiocarbamate, dioctadecyl disulfide, pentaerythritol tetrakis-(β -dodecylmercapto)-propionate.

6. Hydroxylamines, for example, N,N-dibenzylhydroxylamine, N,N-diethylhydroxylamine, N,N-dioctylhydroxylamine, N,N-dilaurylhydroxylamine, N,N-ditetradecylhydroxylamine, N,N-dihexadecylhydroxylamine,

N,N-dioctadecylhydroxylamine, N-hexadecyl-N-octadecylhydroxylamine, N-heptadecyl-N-octadecylhydroxylamine, N,N-dialkylhydroxylamine derived from hydrogenated tallow amine.

7. Nitrones, for example, N-benzyl-alpha-phenyl nitrone, N-ethyl-alpha-methyl nitrone, N-octyl-alpha-heptyl nitrone, N-lauryl-alpha-undecyl nitrone, N-tetradecyl-alpha-tridecyl nitrone, N-hexadecyl-alpha-pentadecyl nitrone, N-octadecyl-alpha-heptadecylnitron, N-hexadecyl-alpha-heptadecyl nitrone, N-octadecyl-alpha-pentadecyl nitrone, N-heptadecyl-alpha-heptadecyl nitrone, N-octadecyl-alpha-hexadecyl nitrone, nitron derived from N,N-dialkylhydroxylamine derived from hydrogenated tallow amine.

8. Polyamide stabilizers, for example copper salts in combination with iodides and/or phosphorus compounds and salts of divalent manganese.

9. Basic co-stabilizers, for example, melamine, polyvinylpyrrolidone, dicyandiamide, triallyl cyanurate, urea derivatives, hydrazine derivatives, amines, polyamides, polyurethanes, alkali metal salts and alkaline earth metal salts of higher fatty acids for example Ca stearate, Zn stearate, Mg stearate, Na ricinoleate and K palmitate, antimony pyrocatecholate or zinc pyrocatecholate.

10. Nucleating agents, for example, 4-tert-butyl-benzoic acid, adipic acid, diphenylacetic acid.

11. Fillers and reinforcing agents, for example, calcium carbonate, silicates, glass fibers, asbestos, talc, kaolin, mica, barium sulfate, metal oxides and hydroxides, carbon black, graphite.

12. Other additives, for example, plasticizers, lubricants, emulsifiers, pigments, optical brighteners, flameproofing agents, anti-static agents, blowing agents and thiosynergists such as dilauryl thiodipropionate or distearyl thiodipropionate.

The phenolic antioxidant of particular interest is selected from the group consisting of n-octadecyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate, neopentantetrayl tetrakis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate), di-n-octadecyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)isocyanurate, thiodiethylene bis(3,5-di-tert-

butyl-4-hydroxyhydrocinnamate), 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene, 3,6-dioxaoctamethylene bis(3-methyl-5-tert-butyl-4-hydroxyhydrocinnamate), 2,6-di-tert-butyl-p-cresol, 2,2'-ethylidene-bis(4,6-di-tert-butylphenol), 1,3,5-tris(2,6-dimethyl-4-tert-butyl-3-hydroxybenzyl)isocyanurate, 1,1,3,-tris(2-methyl-4-hydroxy-5-tert-butylphenyl)butane, 1,3,5-tris[2-(3,5-di-tert-butyl-4-hydroxyhydrocinnamoyloxy)ethyl]isocyanurate, 3,5-di-(3,5-di-tert-butyl-4-hydroxybenzyl)mesitol, hexamethylene bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate), 1-(3,5-di-tert-butyl-4-hydroxyanilino)-3,5-di(octylthio)-s-triazine, N,N'-hexamethylene-bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamamide), calcium bis(ethyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate), ethylene bis[3,3-di(3-tert-butyl-4-hydroxyphenyl)butyrate], octyl 3,5-di-tert-butyl-4-hydroxybenzylmercaptoacetate, bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamoyl)hydrazide, and N,N'-bis[2-(3,5-di-tert-butyl-4-hydroxyhydrocinnamoyloxy)-ethyl]-oxamide.

A most preferred phenolic antioxidant is neopentetetrayl tetrakis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate), n-octadecyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate, 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)isocyanurate, 2,6-di-tert-butyl-p-cresol or 2,2'-ethylidene-bis-(4,6-di-tert-butylphenol).

The laminated thermoplastics produced in this invention may be used as is, e.g. double walled polycarbonate sheet, or further processed into finished articles.

The following examples are for the purpose of illustration only and are not to be construed to limit the nature or scope of the instant invention in any manner whatsoever.

Examples 1-4

The following examples demonstrate the superiority of the o-hydroxyphenyl-s-triazines of the instant invention over the bisbenzotriazoles of U.S. Patent No. 5,108,835 and other structurally related o-hydroxyphenyl-s-triazines in a laminated polycarbonate plaque wherein the UV absorber is incorporated only into the thin surface protecting layer such as prepared in a coextruded article.

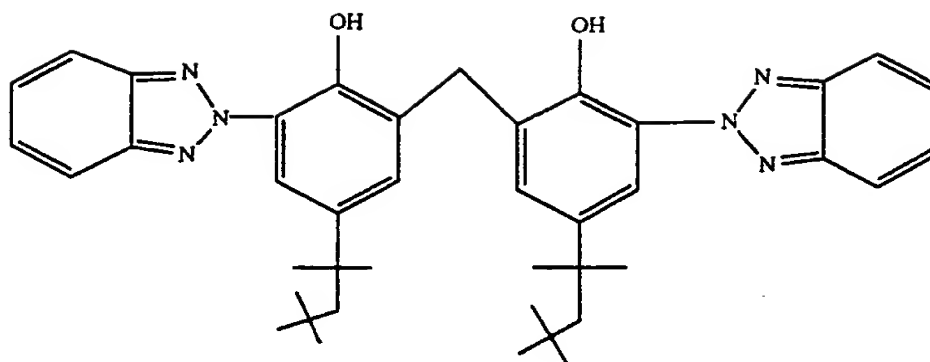
Laminated plaques are prepared by bonding a 1 mil (0.0254 mm) polycarbonate film (LEXAN[®] 145-111N), General Electric Co.) containing 5% by weight of an UV absorber to a non-UV stabilized 125 mil (3.18 mm) polycarbonate plaque (LEXAN[®] 145-111N) via compression molding in a Wabash Compression molder at 280°F (138°C) for 1.8 minutes at 76 psi (4 Kg/cm²), two minutes at 1500 psi (105 Kg/cm²), and then two minutes at 1500 psi (105 Kg/cm²) while cooling. The plaques are then exposed in an Atlas CI-65 Xenon Arc Weatherometer, using the ASTM designation G26-90 Test Method 3 with the protective layer facing the incident light. Polymer degradation is determined by measuring yellowness index (YI) on an ACS spectrophotometer.

The following table shows the number of hours of exposure needed to give an increase in YI of 2 units in the laminates. The data clearly demonstrate the pronounced superiority of the o-hydroxyphenyl-s-triazines of formula I of the instant invention in this method of polymer stabilization versus the current status of the art.

<u>Example*</u>	<u>Hours to Δ YI of 2 units</u>
1	110
2	1450
3	1300
4	2210

*Example 1 is a control and contains no UV absorber in the protective layer.

Example 2 contains in the protective layer 5% of the bisbenzotriazole of U.S. Patent No. 5,108,835 of the formula.



Example 3 contains in the protective layer 5% of the 2,4-di(2,4-dimethylphenyl)-6-(2-hydroxy-4-octyloxyphenyl)-s-triazine.

Example 4 contains in the protective layer 5% of the 2,4-diphenyl-6-(2-hydroxy-4-hexyloxyphenyl)-s-triazine.

Examples 5-7

The following examples demonstrate the superiority of the o-hydroxyphenyl-s-triazines of the instant invention over the bisbenzophenones of U.S. Patent No. 5,306,456 in a laminated polycarbonate plaque wherein the UV absorber is incorporated only into the thin surface protecting layer such as prepared in a coextruded article.

Laminated plaques are prepared by bonding a 1 mil (0.0254 mm) polycarbonate film (LEXAN[®] 141-111N), General Electric Co.) containing 5% by weight of an UV absorber to a non-UV stabilized 125 mil (3.18 mm) polycarbonate plaque (LEXAN[®] 141-111N) via compression molding in a Wabash Compression molder at 350°F (177°C) for three minutes at 1000 psi (70 Kg/cm²), three minutes at 3000 psi (210 Kg/cm²), and then three minutes at 3000 psi (210 Kg/cm²) while cooling. The plaques are then exposed in an Atlas CI-65 Xenon Arc Weatherometer, using the ASTM designation G26-88 Test Method C with the protective layer facing the incident light. Polymer degradation is determined by measuring yellowness index (YI) on an ACS spectrophotometer.

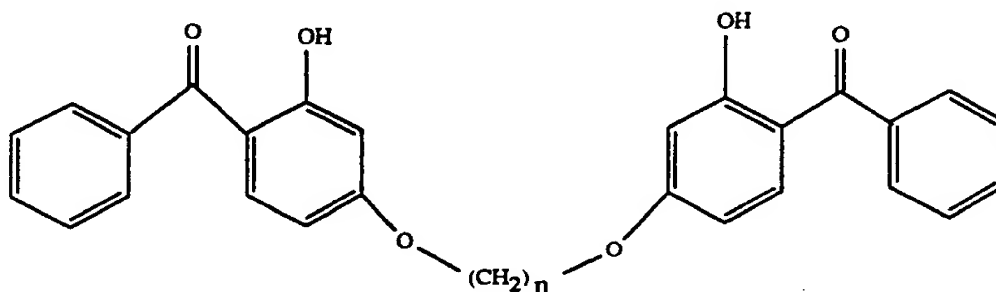
The following table shows the number of hours of exposure needed to give an increase in YI of 2 units in the laminates. The data clearly demonstrate the pronounced

superiority of the o-hydroxyphenyl-s-triazines of formula I of the instant invention in this method of polymer stabilization versus the current status of the art.

<u>Example*</u>	Hours to <u>Δ YI of 2 units</u>
5	80
6	1240
7	1440

*Example 5 is a control and contains no UV absorber in the protective layer.

Example 6 contains in the protective layer 5% of the bridged bisbenzophenone of U.S. Patent No. 5,306,456 of the formula where $n = 10$.

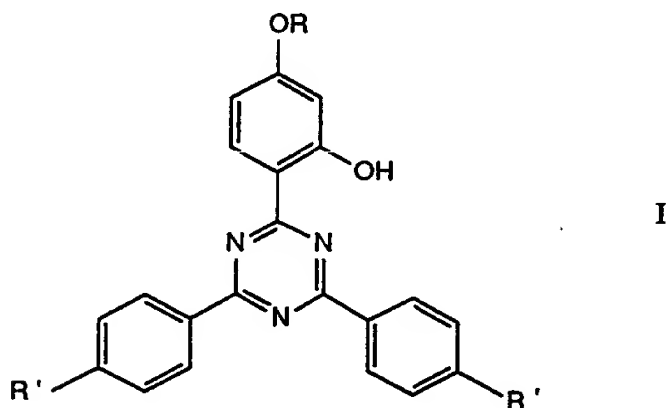


Example 7 contains in the protective layer 5% of the 2,4-diphenyl-6-(2-hydroxy-4-hexyloxyphenyl)-s-triazine.

WHAT IS CLAIMED IS:

1. A process for stabilizing a multi-layered, thermoplastic article, prepared by coextrusion, which process comprises

incorporating into the outer UV absorbing coating layer an effective stabilizing amount of a o-hydroxyphenyl-s-triazine UV absorber of formula I



wherein

R is hydrogen, C₁-C₁₈alkyl, C₂-C₆alkyl substituted by halogen or by C₁-C₁₂alkoxy, or R is benzyl, and

R' is hydrogen or methyl.

2. A process according to claim 1 wherein R is C₁-C₁₂alkyl or benzyl.
3. A process according to claim 1 wherein R is C₃-C₆alkyl.
4. A process according to claim 1 wherein R' is hydrogen.
5. A process according to claim 1 wherein the compound of formula I is 2,4-diphenyl-6-(2-hydroxy-4-hexyloxyphenyl)-s-triazine.
6. A process according to claim 1 wherein the thermoplastic article is coated with a thermoplastic layer 5-500 microns thick, in which said layer contains 0.1% to 20% by weight of the o-hydroxy-phenyl-s-triazine UV absorber.

7. A process according to claim 6 wherein said layer contains 1% to 15% by weight of the o-hydroxy-phenyl-s-triazine.

8. A process according to claim 7 wherein said layer contains 2% to 10% by weight of the o-hydroxy-phenyl-s-triazine.

9. A process according to claim 1 wherein the thermoplastic article and the coating layer are of the same thermoplastic resin or different thermoplastic resins.

10. A process according to claim 9 wherein the thermoplastic resin is selected from the group consisting of aromatic polycarbonates, polyesters, polyester carbonates, polyphenylene oxide, polyvinyl chloride, polypropylene, polyethylene, polyacrylates, polymethacrylates and copolymers and blends which are styrene and acrylonitrile on polybutadiene and styrene and maleic anhydride.

11. A process according to claim 10 wherein the thermoplastic resin is a polycarbonate based on a dihydric phenol selected from the group consisting of 2,2-bis-(4-hydroxyphenyl)propane (bisphenol A); 2,4-bis-(4-hydroxyphenyl)-2-methylbutane; 1,1-bis-(4-hydroxyphenyl)cyclohexane; 2,2-bis-(3-chloro-4-hydroxyphenyl)propane; 4,4'-sulfonyldiphenol; and 1,1-bis-(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane.

12. A process according to claim 11 wherein the thermoplastic resin for both the article and the coating layer is a polycarbonate based on bisphenol A.

13. A stabilized thermoplastic article prepared and stabilized by the process according to claim 1.



Application No: GB 9512540.7
Claims searched: 1-13

Examiner: J P Leighton
Date of search: 6 September 1995

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK CI (Ed.N): B5A(AC, AT17P)

Int CI (Ed.6): B29C(47/06, 67/24)

Other: Online: WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
Ya	GB 2028228 A	Rohm GMBh - see page 2 lines 11-57	All
Ya	GB 1572728 A	Dynamit Nobel AG - whole disclosure	"
Ya	GB 1444562 A	Dynamit Nobel AG - see page 2 lines 8-20	"
Yb	US 5288778 A	Ciba-Geigy Corporation - whole disclosure	"
Yb	US 3244708 A	Ciba Limited - whole disclosure	"

X Document indicating lack of novelty or inventive step
Y Document indicating lack of inventive step if combined with one or more other documents of same category.

& Member of the same patent family

A Document indicating technological background and/or state of the art.
P Document published on or after the declared priority date but before the filing date of this invention.
E Patent document published on or after, but with priority date earlier than, the filing date of this application.